The Patent Office

24 FEBRUARY 2000

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ts Form 1/77

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26 FEB 1999

26FEB99 E428504-2 002838
P01/7700 0.00 - 9904427.3

# Request for grant of a patent

*(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)*

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

BKVD/JMS/DBN.99

2. Patent application number
*(The Patent Office will fill in this part)*

**9904427.3**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Trikon Holdings Limited
Coed Rhedyn
Ringland Way
Newport
Gwent.
NP6 2TA

Patents ADP number *(if you know it)*

7435423001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

Method Treating an Insulating Layer

5. Name of your agent *(if you have one)*

Wynne-Jones, Laine & James

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

22 Rodney Road
Cheltenham
Gloucestershire
GL50 1JJ

Patents ADP number *(if you know it)*

1792001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

| Country | Priority application number *(if you know it)* | Date of filing *(day / month / year)* |
|---|---|---|
| -- | -- | -- |

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

| Number of earlier application | | Date of filing *(day / month / year)* |
|---|---|---|
| -- | -- | -- |

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

*a) any applicant named in part 3 is not an inventor, or*
*b) there is an inventor who is not named as an applicant, or*
*c) any named applicant is a corporate body.*
*See note (d))*

Yes

**Pat[illegible]'s Form 1/77**

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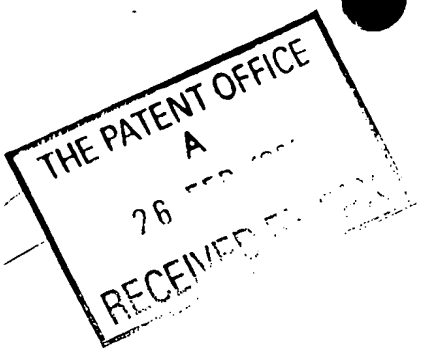


| | |
|---|---|
| Continuation sheets of this form | |
| Description | 7 |
| Claim(s) | 2 |
| Abstract | – |
| Drawing(s) | 5 |

10. If you are also filing any of the following, state how many against each item.

| | |
|---|---|
| Priority documents | – |
| Translations of priority documents | – |
| Statement of inventorship and right to grant of a patent *(Patents Form 7/77)* | – |
| Request for preliminary examination and search *(Patents Form 9/77)* | – |
| Request for substantive examination *(Patents Form 10/77)* | – |
| Any other documents *(please specify)* | – |

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 26/2/99

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. B.K.C. Dunlop - (01242) 515807

**Warning**

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**Notes**

*a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*

*b) Write your answers in capital letters using black ink or you may type them.*

*c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

*d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

*e) Once you have filled in the form you must remember to sign and date it.*

*f) For details of the fee and ways to pay please contact the Patent Office.*

# Method Treating an Insulating Layer

This invention relates to a method of treating an insulating layer such as found in semi-conductor devices.

As the designers of semi-conductor architecture push the devices within the semi-conductors closer and closer together, the permittivity of the insulating layers which are formed between the connecting metal tracks, becomes more significant. The trend is therefore to produce insulating materials with lower and lower dielectric constants (k). One approach to forming such materials is to introduce carbon into the insulating material and such a method is described in our co-pending International Patent Application PCT/GB97/02240, the disclosure of which is incorporated herein by reference.

In order to form the metal tracks separated by the insulating layer or to connect those tracks to other tracks or devices formed in the semi-conductor material on which the insulating layers are deposited, it is necessary to etch into or through the insulating layer and subsequently fill those recesses with electrically conducting metal. Such recesses are generally formed by coating the upper surface of the insulating layer with a photo-resist, removing certain parts of the resist using photo-lithographic techniques, etching through the exposed openings in the resist to form the recesses and then removing the layer of resist by reactively etching the resist using oxygen.

However, it has been found that where the insulating

layer contains carbon, the dielectric constant increases as a result of the reactive oxygen etching, the side walls of the formation are etched creating barrelling and there are subsequent problems with filling the recesses with metal.

From one aspect the invention consists in a method of treating an insulating layer in which a formation has been etched through a layer of resist comprising reactive etching the resist, inhibiting the absorption or removing water vapour and/or oxygen at the exposed surfaces of the etch formation and filling the formation with conductive metal in the absence of said water vapour and/or oxygen.

The inhibiting step may include supplying hydrogen with or to an etchant gas, e.g. oxygen, and/or it may comprise supplying nitrogen with or to the etchant gas. Preferably the step of inhibiting includes supplying a gas which is the source of reactive hydrogen and/or nitrogen with or to the etchant gas. In one embodiment the gas may be $NH_3$. Where the etchant gas is oxygen, the ratio of oxygen to the gas may be approximately 3:1 and similar ratios may be appropriate with other etchant gases.

In an alternative arrangement the inhibiting step may be performed by maintaining the substrate under vacuum until the metallisation step is completed or there may be a removal step including heating the insulating layer prior to metallisation to outgas the insulating material.

Preferably the insulating layer has a dielectric constant of less than 4 and/or includes carbon. More particularly the dielectric constant is below 3.5 and most

preferably below 3.0.

The carbon concentration in the dielectric film is most preferably more than 10%.

Although the invention has been defined above it is to be understood it includes any inventive combination of the steps set out above or in the following description.

The invention may be performed in various ways and specific examples will now be described, by way example, with reference to the accompanying drawings, in which:

Figure 1 is a vertical section or view through apparatus for performing the method;

Figure 2 is a view of an insulating layer with a number of vias filled using prior art techniques;

Figure 3 is an enlargement of the vias of Figure 3;

Figure 4 is a view of vias filled utilising the steps of the present invention; and

Figure 5 is an enlargement of a single via.

Referring to Figure 1 a vacuum chamber 10 includes a wafer support 11 for supporting a wafer opposite a plasma source 12 through which reactive gas can be streamed via gas inlet 13. A heating lamp 14 is provided for heating the wafer 16 and the chamber can be evacuated via a high vacuum valve 15. A plasma is generated remotely from the wafer in the plasma tube by means of an RF coil 17.

Subsequent to etching the dielectric layer, a wafer 16 is placed upon the support 11 and, in the prior art arrangement, oxygen is streamed into the chamber through the plasma tube 12 and reactively etches the photo-resist on the

previously been described.

The following experiment was performed:

In order to remove photo-resist and strip back anti-reflective coating materials the above described process was run initially using oxygen only and then using a gas mixture including $NH_3$.

The following conditions applied:

Oxygen only process (conventional resist strip)

150mm wafer using 1kw lamp

| | Step 1 | Step 2 |
|---|---|---|
| Gas Flow: | 496 sccm $O_2$ | 496 sccm $O_2$ |
| Pressure: | 750 mT | 750 mT |
| Plasma power: | 500 W ICP | 500 W ICP |
| Lamp heater: | 80% lamp power | 45% lamp power |
| Process time: | 60 sec's | 120 sec's |

Ammonia containing process (embodiment of the invention)

150mm wafer using 1kw lamp

| | Step 1 | Step 2 |
|---|---|---|
| Gas Flows: | 496 sccm $O_2$ | 496 sccm $O_2$ |
| | 50 sccm $N_2$ | 50 sccm $N_2$ |
| | 150 sccm $NH_3$ | 150 sccm $NH_3$ |
| Pressure: | 750 mT | 750 mT |
| Plasma power: | 500 W ICP | 500 W ICP |
| Lamp heater: | 80% | 45% |
| Process time: | 40 sec's | 90 sec's |

[ICP : Inductively Coupled Plasma]

Actual temperatures of the substrate was not measured but estimated at ~ 250°C.

Subsequently to metallise via holes with barrier/contact layers and aluminium the following process was run:

| | | |
|---|---|---|
| Preheat: 1.5kW, 5 mins | | |
| Barrier deposition: | Ti/TiN | 300A/700A deposited at 200°C |
| Aluminium alloy deposition: | Al/0.5%Cu | 1 micron deposited at 450°C |
| Forcefill®: | 440°C,1 min | 1200 bar inlet pressure<br>720 bar chamber pressure |

(Forcefill is the Registered Trade Mark for a metallisation process described in our European Application Patent No. 92304633.8 and U.S. Patent 5527861, which are incorporated by reference)

Using the above metallisation process 100% of via holes were filled with the ammonia resist strip process and 70% of via holes were filled with the oxygen only resist strip process. It is also known that a commercial tungsten plug preceded by barrier/contact layers also suffered from unreliable via hole filling when the dielectric contained carbon and a conventional resist strip process was carried out without the further processing according to this invention.

Figures 2 and 3 and 4 and 5 are SEM's of the oxygen only and the gas mixture processes respectively. In these SEM's the bright areas represent voids and it will be seen that the conventional metallisation process is rather unsuccessful. In contrast the gas mixture approach provides good metallisation.

It is not fully understood why the standard oxygen plasma resist strip process creates metallisation problems nor why the introduction of ammonia resolves them. However it is a problem widely known by those attempting to integrate low k dielectric materials, particularly within C>10% containing dielectrics. It is possible that carbon is removed during the oxygen reactive etching leaving the exposed surface of the formation vulnerable to attack and contamination e.g. by water vapour being absorbed during subsequent atmospheric exposure. Such exposure generally takes place, because photo-resist removing stations and metallisation stations are manufactured as independent units. However, if this analysis is correct, it is conceivable that the benefits seen above could also be obtained either by significant heating, for example under vacuum, to outgas the insulating layer prior to metallisation or by maintaining the wafer in vacuum between the resist stripping process and the completion of the metallisation process. The pre-heating option is not commercially desirable both for thermal budget reasons and because it will slow throughput.

It is hypothesed that the introduction of ammonia into

the oxygen may overcome the problems of the oxygen only process because the hydrogen from the ammonia replaces the carbon removed by the oxygen by attaching to the dangling silicon bonds. This substitution of the hydrogen for the removed carbon thus stabilises the dielectric structure and guards against subsequent water vapour and absorption. Additionally or alternatively the nitrogen may replace the carbon or there may be an as yet unidentified interaction of the hydrogen and nitrogen in a carbon replacement process.

Additionally or alternatively the presence of hydrogen and/or nitrogen may inhibit the actual replacement of carbon by oxygen.

It is possible that the nitrogen/hydrogen treatment step may be carried out separately prior to the metallisation step, although once again this is probably a less attractive solution for reasons of throughput.

## Claims

1. A method of treating an insulating layer in which a formation has been etched through a layer of resist comprising reactive etching the resist, inhibiting the absorption of or removing water vapour and/or oxygen at the exposed surfaces of the etched formation and filling the formation with conductive metal in the absence of said water vapour and/or oxygen.

2. A method as claimed in claim 1 wherein the inhibiting step includes supplying hydrogen with or to a reactive etchant gas.

3. A method as claimed in claim 1 or claim 2 wherein the inhibiting step includes supplying nitrogen with or to a etchant gas.

4. A method as claimed in claim 1 wherein the step of inhibiting includes supplying a gas which is a source of reactive hydrogen and/or nitrogen with or to a reactive etchant gas.

5. A method as claimed in claim 4 wherein the gas is $NH_3$.

6. A method as claimed in claim 4 or claim 5 wherein the ratio of oxygen to the gas is approximately 3:1.

7. A method as claimed in claim 1 wherein the inhibiting step is performed by maintaining the substrate under vacuum until the metallisation step is completed.

8. A method as claimed in claim 1 wherein the removal step includes heating the insulating layer prior to metallisation.

9. A method as claimed in any one of the preceding claims wherein the insulating layer has a dielectric constant of less than 4.

10. A method as claimed in any one of the preceding claims wherein the insulating layer includes carbon.

11. A method as claimed in claim 10 wherein dielectric layer includes more than 10% carbon.

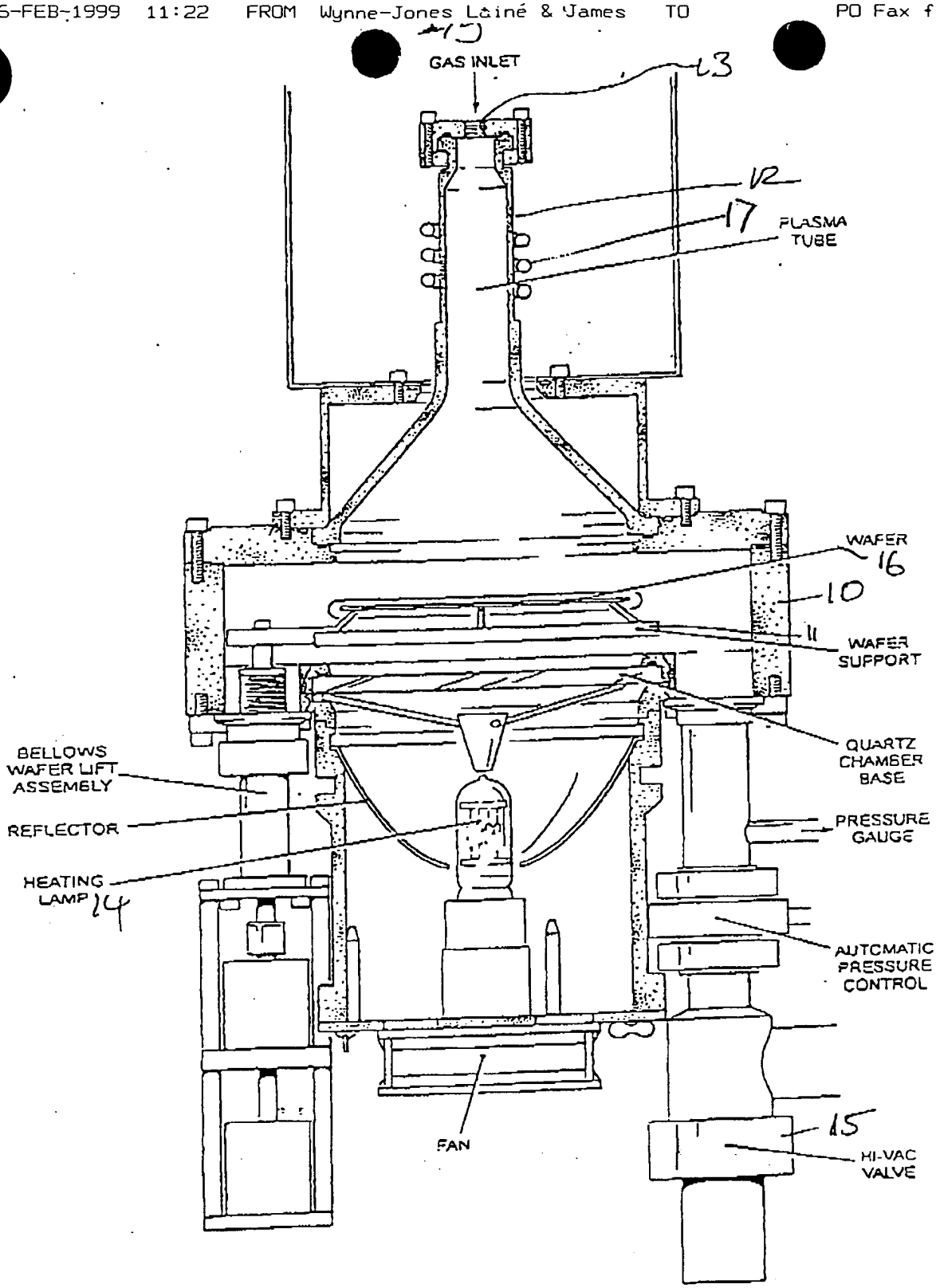
GAS INLET
13
12
17
PLASMA TUBE
WAFER
16
10
11
WAFER SUPPORT
QUARTZ CHAMBER BASE
BELLOWS WAFER LIFT ASSEMBLY
REFLECTOR
PRESSURE GAUGE
HEATING LAMP
14
AUTOMATIC PRESSURE CONTROL
FAN
15
HI-VAC VALVE

FIG 1

215

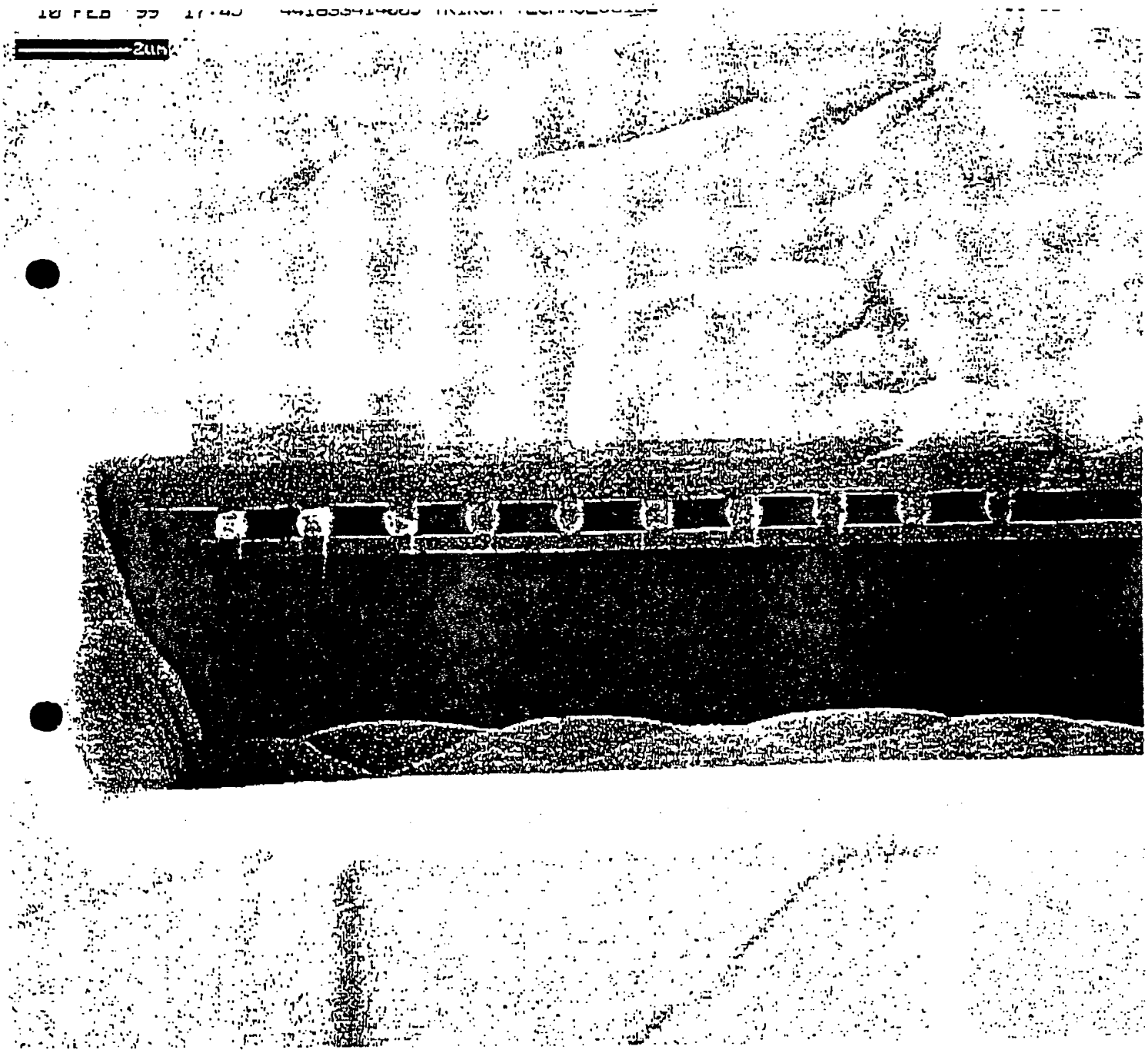


FIG2

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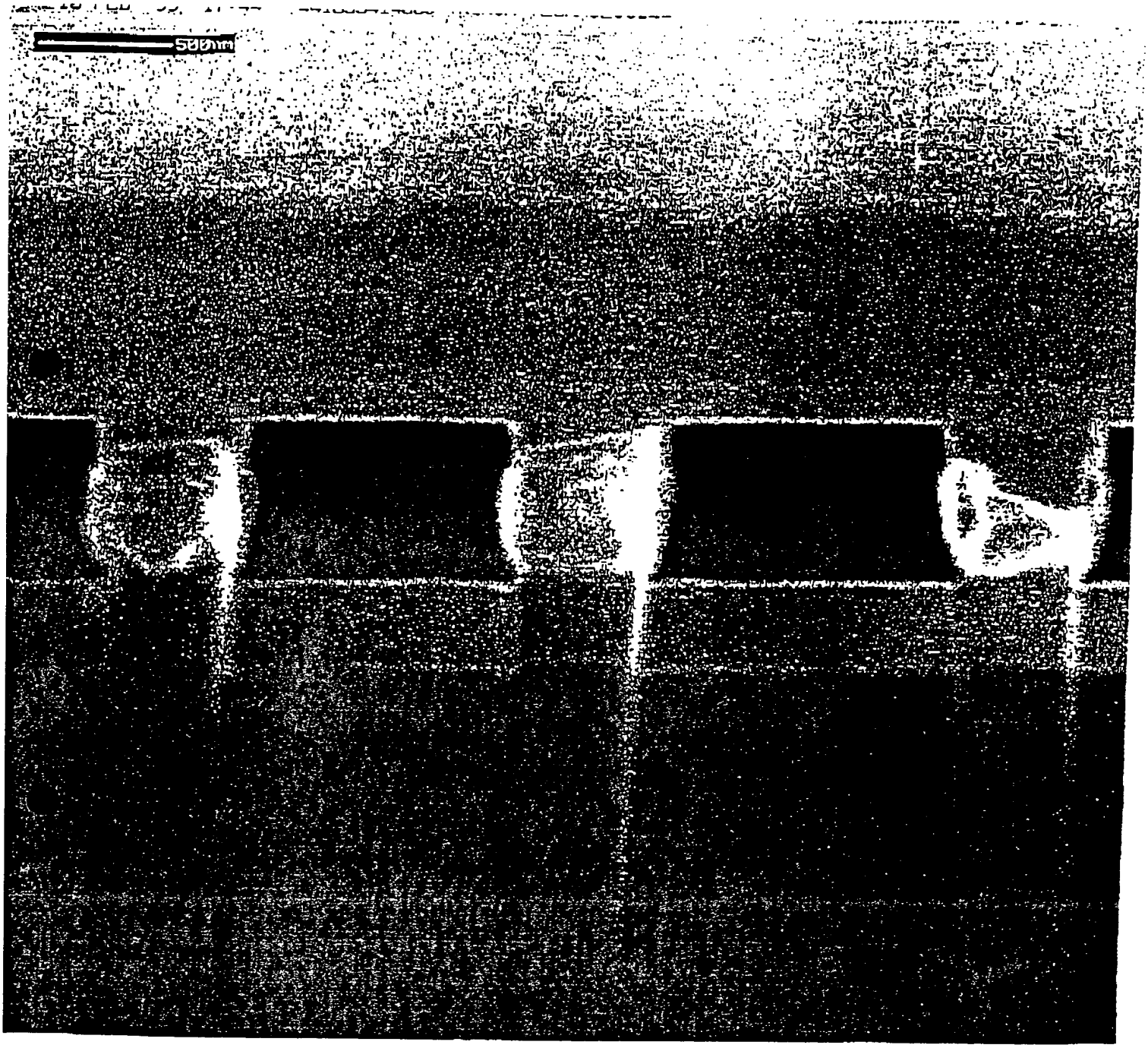


FIG3.

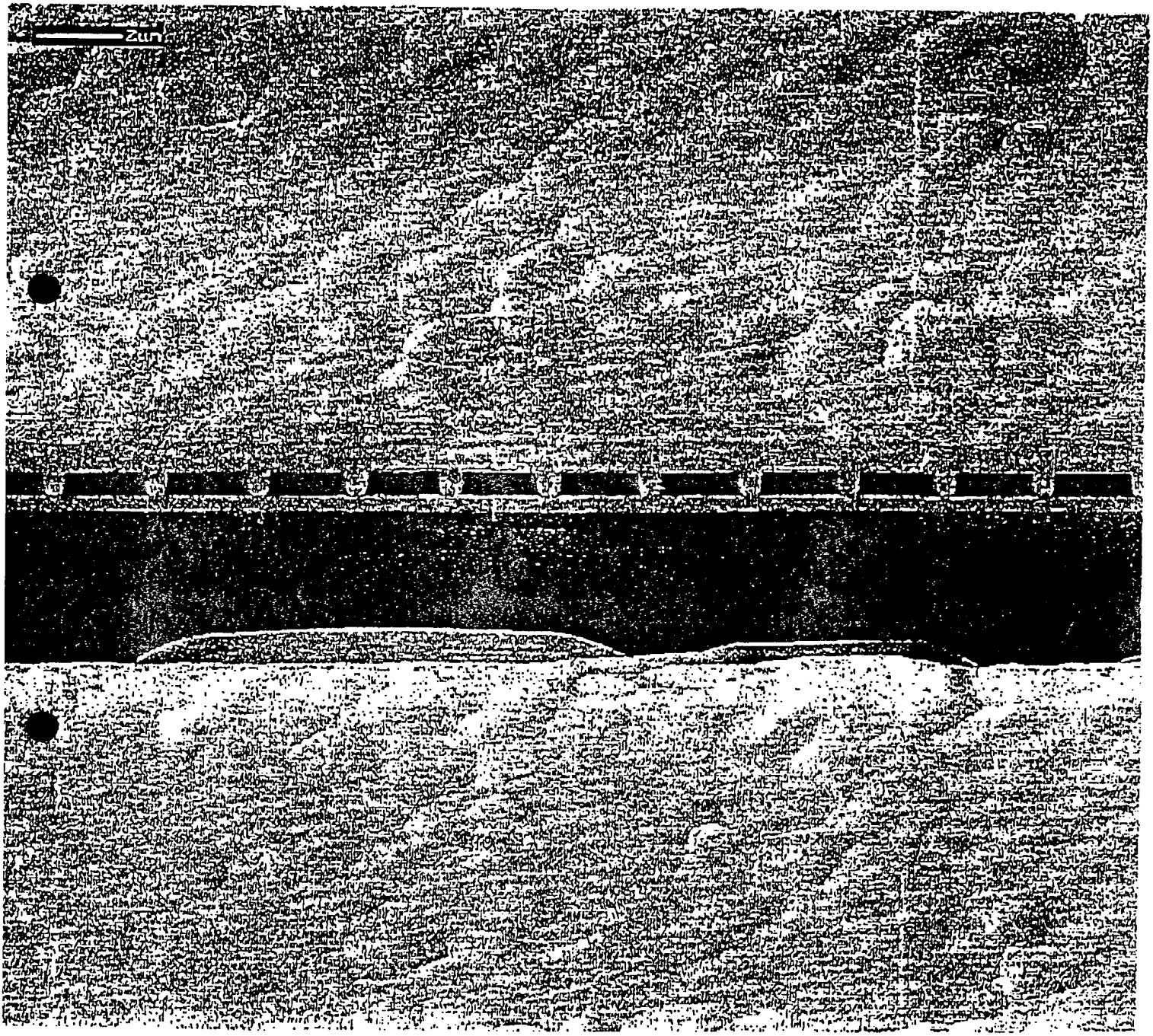


FIG 4

5/5.

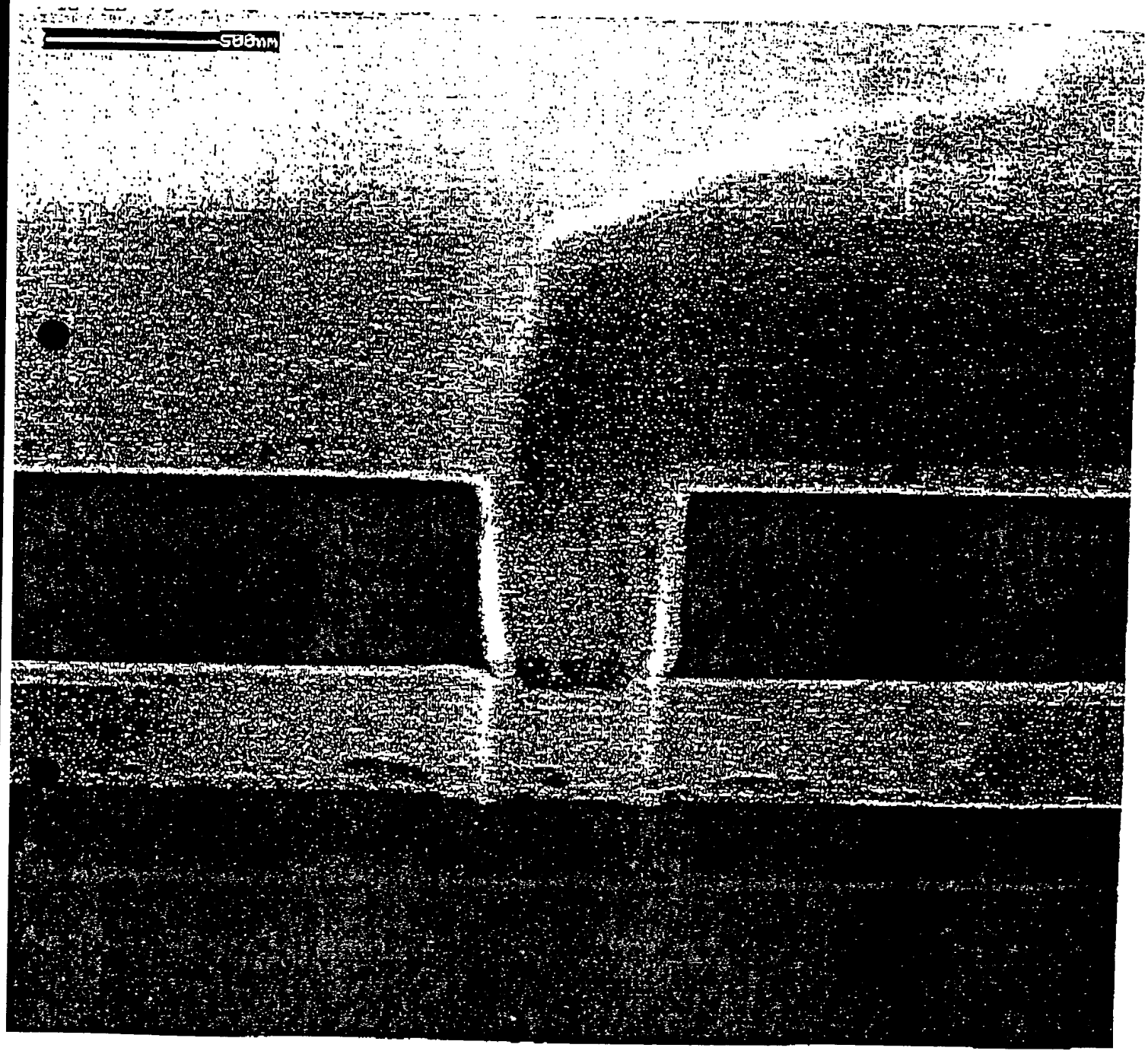


FIG5